Using Pencil Drawing To Pattern Robust Superhydrophobic Surfaces To Control the Mobility of Water Droplets

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ABSTRACT: For centuries, pencils have been convenient implements for writing, drawing, and portraying. In this study, we found another use for the lowly pencil: to modulate the mobility of water droplets on a robust superhydrophobic surface. Here, we describe a simple method for fabricating durable superhydrophobic films from carbon nanotube (CNT)/polybenzoxazine coatings. These as-prepared coatings possessed robust superhydrophobicity with strong adhesion to glass and metal substrates. We achieved tunable water droplet mobility on the superhydrophobic surface with patterned wettability after drawing with a pencil. The mobility could be switched rapidly (within 1 min) between the poorly adhesive rolling state and the highly adhesive pinning state through sequential pencil drawing and sonication processes.
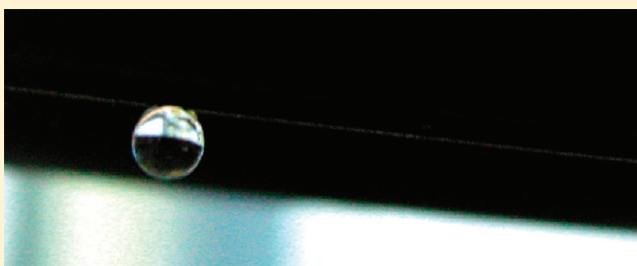
■ INTRODUCTION

Water repellency of a solid surface is one of the most challenging subjects for both fundamental research and practical application. The wettability of a solid surface is controlled by its topographical microstructure and surface chemical composition. Using this approach, many effective methods have been developed to prepare a variety of superhydrophobic surfaces.[1−7] One path toward artificial superhydrophobic surfaces, by mimicking the structure of the lotus leaf with its micrometer-level surface roughness and covering of branching-like nanostructures, has attracted considerable interest. The high water contact angle (160°) and low sliding angle (2°) of the lotus leaf cause water drops to bead and roll off from the surface, providing extreme water repellency and self-cleaning characteristics.[8] In addition, superhydrophobic surfaces with water adhesive properties (high-adhesion superhydrophobic surfaces) have also drawn a great amount of attention recently. The water droplets on these surfaces feature high static contact angles (>150°), but they are pinned on the surfaces at any tilted angle.[9,10]

High-adhesion superhydrophobic surfaces possess many potential applications, for example, for no-loss microdroplet transportation and microfluid control system and in lab-on-a-chip (LOC) devices.[11−14] Jiang et al. designed the first sticky superhydrophobic surfaces based on polystyrene nanotubes;[15] they also obtained a system exhibiting a switchable transition from the superhydrophobic composite state to the superhydrophobic wetted state.[16] More recently, they realized a patterned wetting-state transition on an aligned ZnO nanorod array surface, based on a photoelectric cooperative wetting process.[17] Zhou et al. used masked UV irradiation to prepare superhydrophobic TiO$_2$

nanotube films exhibiting tunable water-droplet adhesion.[18] By patterning superhydrophobic paper substrates with a high surface free energy ink, Breedveld and co-workers developed an LOC device capable of storing, transferring, mixing, and sampling liquid drops.[14]

Herein, we present a simple method for fabricating robust superhydrophobic surfaces and performing the reversible switching of water droplet mobility on these surfaces through pencil drawing/ultrasonic cleaning cycles. Because many of their applications feature extreme operating conditions, superhydrophobic coatings must exhibit high durability, especially because a surface with high roughness generally has poorer mechanical strength than has a flat surface. Nevertheless, a lack of mechanical durability is a common problem for most reported artificial superhydrophobic surface coatings, limiting their potential commercial applications. In this study, we prepared durable superhydrophobic surface coatings comprising carbon nanotubes (CNTs) and polybenzoxazine, a low surface free energy thermosetting polymer.[19] These CNT/polybenzoxazine coatings possessed robust superhydrophobicity and adhered strongly to glass and metal substrates. Most interesting is that the mobility of water droplets on the CNT/polybenzoxazine coatings could be altered simply by drawing on the surface with a pencil. The resulting graphite residues decreased the surface roughness of those specific regions, transiting the surface from a low-adhesive rolling state to the high-adhesive pinning state on the patterned superhydrophobic
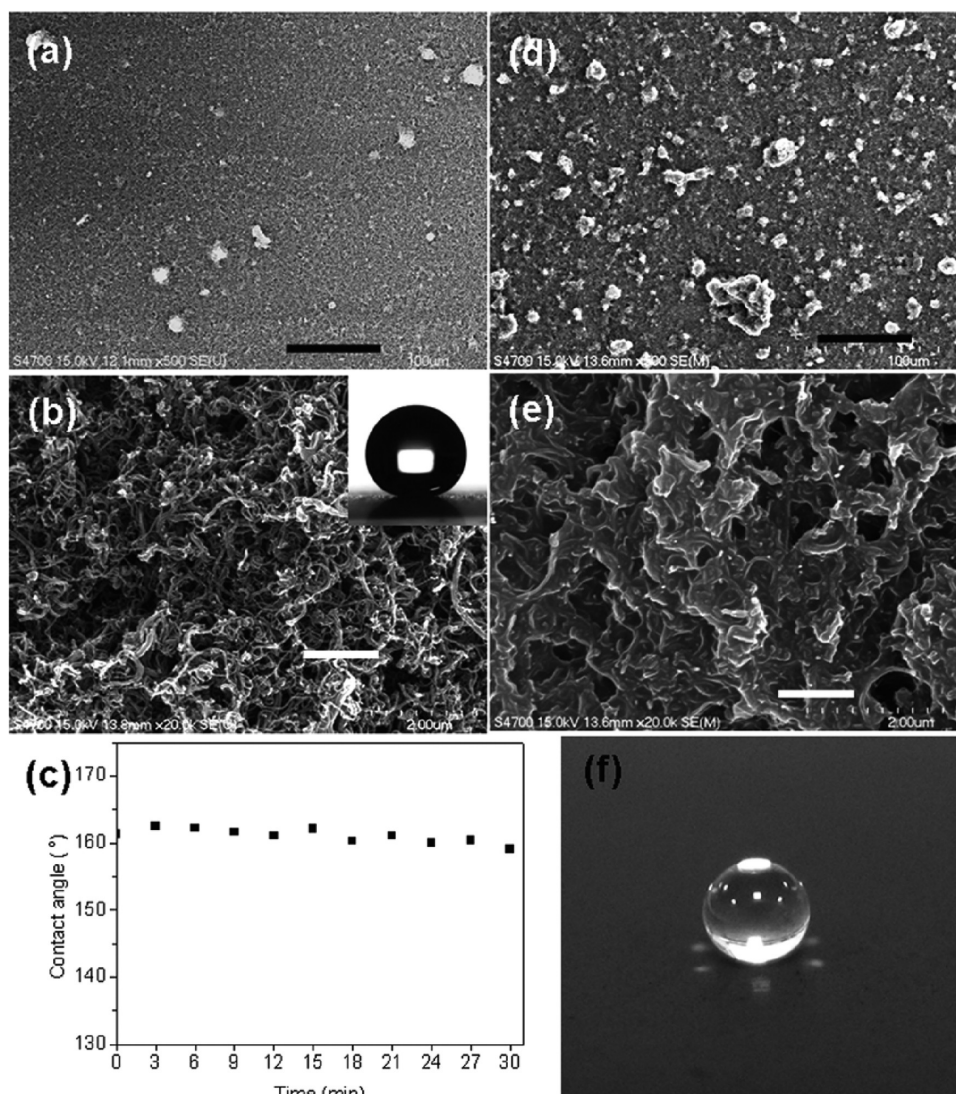
Figure 1. (a) Large-area SEM image of the superhydrophobic surface of sample 1 on a glass slide. Scale bar: 50 μm. Inset: photograph of a water droplet on sample 1. (b) Enlarged view of a microstructure in (a); scale bar: 1 μm. (c) Time dependence of the water contact angle for sample 1. (d) Large-area SEM image of sample 2; scale bar: 50 μm. (e) Enlarged view of a microstructure in (d); scale bar: 1 μm. (f) Optical image of a water droplet on sample 2.

surfaces. To the best of our knowledge, this method is the simplest one reported for controlling the mobility of water droplets on superhydrophobic coatings. Furthermore, the use of commercially available raw materials and the simple fabrication and operation process makes it possible to apply such surfaces in academic research and industrial applications.

■ EXPERIMENTAL SECTION

2,2-Bis(3-phenyl-3,4-dihydro-2*H*-1,3-benzoxazinyl)propane (BA-a benzoxazine) was supplied by Shikoku Chemicals Corp. (Japan). Multiwalled carbon nanotubes (MWCNTs; average diameter: 10−20 nm; length: 5−15 μm) were purchased from Conyuan Biochemical Technology. These materials were used as received. Water that had been purified through reverse osmosis was further purified using a Millipore Milli-Q system.

Superhydrophobic coatings were prepared on a glass slide and Al foil through a two-step process. First, a solution of BA-a benzoxazine (0.5 g) in tetrahydrofuran (THF, 10 mL) was spin-coated (1500 rpm, 45 s) onto a glass slide (or Al foil) using a

photoresist spinner. Next, an MWCNT/EtOH suspension (1 mg/mL, sonicated for 30 min prior to use) was sprayed onto the benzoxazine surface, which was positioned on a heating plate held at ca. 130 °C and then cured in an oven at 220 °C for 1 h. To enhance the durability, the rough MWCNT surfaces were modified with the pure BA-a polybenzoxazine film. The BA-a benzoxazine solution (0.12 g/mL in THF) was filtered through a 200 nm syringe filter and then spin-coated (1500 rpm, 45 s) onto a rough surface; the sample was then cured at 220 °C for 1 h.

The microstructures of the MWCNT/polybenzoxazine hybrid films were characterized using a Hitachi-S-4700 scanning electron microscope (acceleration voltage: 5 kV); each specimen was coated with a thin layer of Pt/Pd prior to observation. Static, advancing, and receding contact angles were measured for 4 μL droplets using a FDSA MagicDroplet-100 contact angle goniometer. The sliding angles were measured at different droplet volumes. Each of the reported contact angles represents the average of six measurements. The pencil hardness of the superhydrophobic films was determined using the method described

in ASTMD 3363, a standard test method for film hardness. The tape test was performed according to ASTM D 3359-02, a standard test for measuring adhesion.

RESULTS AND DISCUSSION

The BA-a benzoxazine was spin-coated onto a glass slide and then the sample was cured at 220 °C for 1 h, providing a smooth BA-a polybenzoxazine film. The water contact angles of the BA-a polybenzoxazine coatings were 108 ± 2°.

Combining BA-a polybenzoxazine with MWCNTs provided superhydrophobic coatings on the glass slides. We sprayed MWCNT/EtOH suspensions onto the BA-a benzoxazine-modified glass slides positioned on a heating plate; we then subjected the samples to curing in an oven. The as-prepared MWCNT/polybenzoxazine coating (sample 1) possessed a high water contact angle (162 ± 2°) and small sliding angle (<2°). Figure 1a,b presents top-view scanning electron microscopy (SEM) images of sample 1. This rough substrate possessed both micro- and nanoscale (binary) features. A few microislands (3−10 μm) were randomly distributed on this surface (Figure 1a), with branchlike nanostructures present on both the microislands and underlying surfaces (Figure 1b) of the rough substrate. Such a morphology dramatically increases the surface roughness and provides a composite interface[20,21] in which air becomes trapped within the grooves beneath the liquid, thereby inducing superhydrophobicity. We evaluated the time dependence of the wettability in terms of the contact angles of pure water; droplets positioned on the superhydrophobic surface possessed near-spherical shapes for over 30 min (the water droplet could still be moved easily at that time), suggesting stable superhydrophobicity.

The poor adhesion strength of this superhydrophobic coating is a serious problem limiting its use in industrial applications. To improve the adhesive strength, we modified the rough MWCNT/polybenzoxazine surface through application of a pure BA-a polybenzoxazine film, optimizing the conditions to ensure that the coating did not cover the entire rough surface. Nevertheless, there was enough polybenzoxazine to cement the MWCNT network to the surface of the glass slide. Figure 1d,e presents SEM images of the modified MWCNT/polybenzoxazine hybrid surface (sample 2) at different magnifications. The BA-a polybenzoxazine coating was present on both the microislands and the underlying surfaces (Figure 1d); the branchlike MWCNT nanostructures were connected together by the polybenzoxazine films (Figure 1e). Sample 2 retained the superhydrophobicity of sample 1, with a high contact angle (160 ± 1°, Figure 1f) and water droplets readily moving when the surface was tilted slightly (sliding angle: 4°). The time dependence of the water contact angle for sample 2 was similar to that observed for sample 1; again, the contact angle of water droplets on sample 2 remained constant for over 30 min.

We used a Scotch tape test, based on the ASTM D3359-02 standard, to investigate the adhesion of these superhydrophobic coatings (samples 1 and 2) to the substrate. In this test, the tape is pressed against the coating and then peeled off. Figure 2a displays an SEM image of sample 1 after performing the tape test; a large number of CNTs had peeled off, with only a few CNT residues remaining on the glass substrate. The absence of CNTs on the resulting composite surface greatly reduced the roughness and, thereby, decreased the hydrophobicity; the water contact angle decreased from 162° to 73°, and the sliding angle increased from 2° to 90°. In contrast, Figure 2b presents the SEM images of
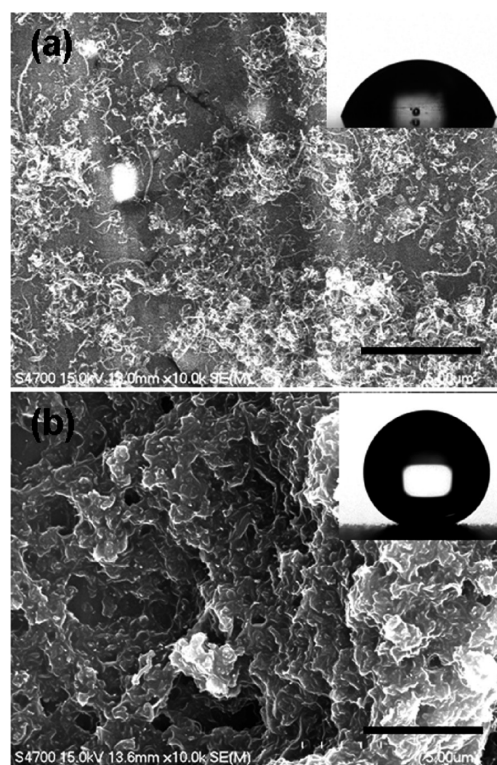

Figure 2. SEM images of (a) sample 1 and (b) sample 2 after performing the tape test. Scale bars: 3 μm. Insets: photographs of water droplets on both samples.

sample 2 after performing the tape test. Compared with the image of the original film (Figure 1e), the surface morphology changed only slightly such that a few microislands removed or damaged by the tape. Therefore, sample 2 adhered relatively strongly to the substrate and retained its superhydrophobicity (contact angle: 155° ± 2°; sliding angle: 6°) after performing the adhesion test.

In general, surface superhydrophobicity is evaluated using a combination of static contact angles and sliding angles. Notably, however, superhydrophobic surfaces, including lotus leaves and artificial materials, often lose their functionality when droplets are squeezed or impacted on them. To further explore the robustness of sample 2, we performed compression experiments[22,23] in which we squeezed a 4 μL water droplet between two identical substrates and then slowly released the pressure, until the initial distance between the plates was restored. The internal pressure was evaluated using the Laplace equation[24]

$$p = 2\gamma|\cos\theta|x^{-1} \qquad (1)$$

where γ is the water surface tension, θ is the contact angle under compression, and x is the distance between the samples. The sequence of photographs in Figure 3a−g reveals that the droplet flattened with the contact angle gradually decreasing from 160 ± 2° to 146 ± 3° during the squeezing stage and then the contact angle recovering progressively from 146 ± 3° to 154 ± 2° during the relaxation stage. Remarkably, a water droplet that had been compressed under a pressure of 194 Pa readily rolled off from the surface of sample 2 when tilted at an angle of 8° (Figure 3h), indicating robust superhydrophobicity within an extended range of compression, making this coating more durable and also usable in more industrial applications.
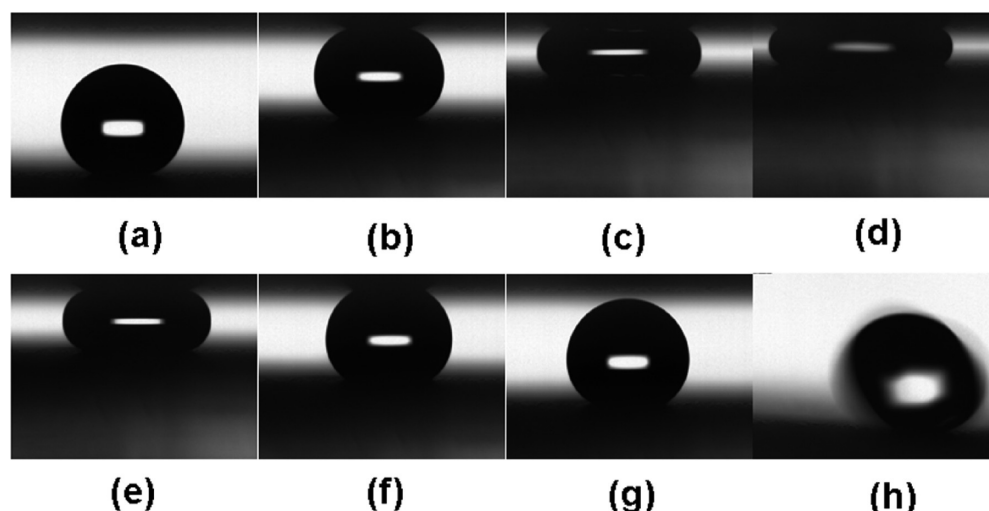
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Figure 3. Behavior of a 4 μL water droplet between two identical substrates covered by a superhydrophobic coating (sample 2): Sequential snapshots for a cycle of compression/relaxation. Image (d) displays the maximum compression state. In image (h), the compressed droplet readily rolled off the surface when tilted at an angle of 8°.
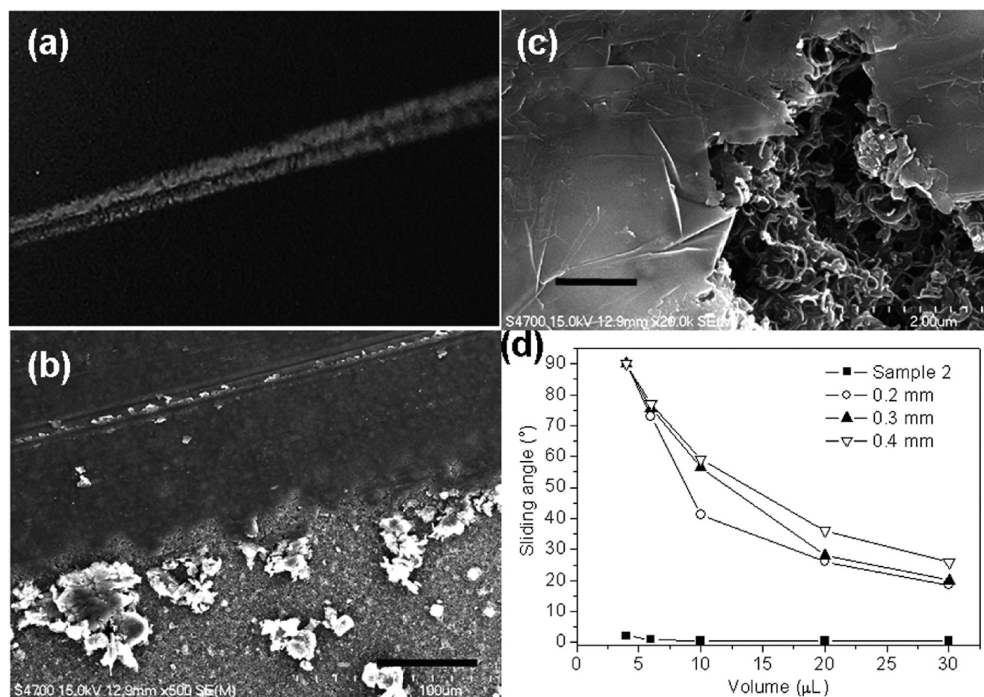

Figure 4. (a) Photograph and (b) SEM image of the graphite residues on sample 2. Scale bar: 50 μm. (c) Enlarged view of (b); scale bar: 1 μm. (d) Plots of slide angles with respect to droplet volume on the patterned substrates (for various line widths) and on a control substrate (sample 2).

A pencil scratch test revealed that the hardness of sample 2, after reinforcing with pure BA-a polybenzoxazine was between F and H; in comparison, sample 1's hardness was between 7B and 5B. Most interesting, we found that the hydrophobicity of the robust superhydrophobic surface was modified after drawing on it with the pencil. The pencil created marks via physical abrasion, leaving behind a trail of graphite residues[25] that adhered to the superhydrophobic surface (Figure 4a). The difference in contact angles between the superhydrophobic coating (sample 2, 160 ± 2°) and homogeneous full-coverage films of graphite (88 ± 2°) was sufficient to form a patterned wettability. Because the type of graphite pencil did not significantly influence the wettability, we used the 2B graphite pencil for our following experiments. Figure 4b,c presents top-view SEM images, at different magnifications, of sample 2 after pencil scratching; we observed the presence of graphitic residues on the superhydrophobic surfaces. Magnified SEM images of the graphitic residues revealed smooth surfaces, greatly reducing the surface roughness in specific regions and increasing the contact area between the solid and the liquid when we placed a water droplet on the surface. We obtained patterned substrates by using 2B graphite pencil to draw hydrophobic lines on the superhydrophobic surface (sample 2).
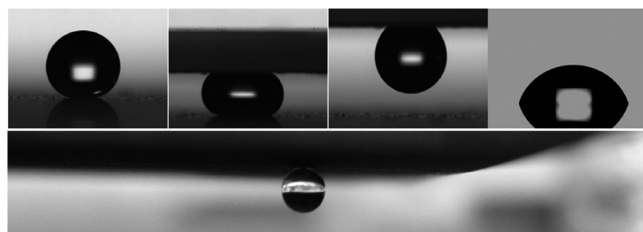
Figure 5. Photographs of the transfer of a water droplet from a super-hydrophobic surface to a hydrophilic one.
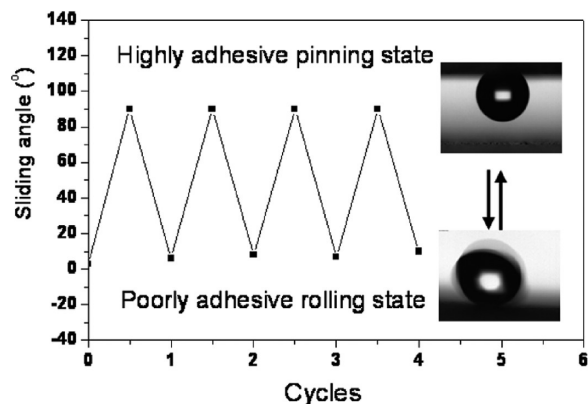

Figure 6. Reversibility of the water droplet adhesion strength of sample 2 after alternating the pencil drawing and sonication steps for several cycles.

Figure 4c displays the sliding angle (angle at which the drop started to slide in the vertical direction of the hydrophobic line) plotted with respect to the drop volume for different line widths, along with the sliding angles of blank superhydrophobic surface. Data points that mark the sliding angle of 90° represent the droplets that were pinned to the substrates even when tilted vertically or flipped upside down. As expected, for each substrate, the sliding angle decreased upon increasing the volume of the droplet. A comparison of the results obtained for the patterned and blank substrates reveals that at a constant drop volume (V) the sliding angle increased upon increasing the line width. Surface exhibiting adequately high adhesion to liquids would have many potential applications, for example, in liquid transportation without loss and in the analysis of liquid samples with very small volumes. Our patterned superhydrophobic surface can be used as a "mechanical hand" to transfer small water droplets from a superhydrophobic surface to a hydrophilic one. The photographs in Figure 5 reveal the transfer of a water droplet from an ordinary superhydrophobic surface (sample 2; water contact angle: 161°) to a patterned superhydrophobic surface, through touching and adhering to this water droplet until it was fully transferred from the ordinary superhydrophobic surface. Finally, we released this water droplet onto a hydrophilic surface [a poly(4-vinylphenol) thin film].

The water droplet mobility on the patterned superhydrophobic surface could be recovered to a rolling state through a rapid process. Figure 4b reveals that the robust superhydrophobic surface (sample 2) maintained its microstructure after performing the pencil scratching test; the graphitic residues merely sat on the surface and did not cause any significant damage to the

microstructures. We removed the graphitic residues through sonication process using a solvent, *n*-hexane, possessing a relatively low surface tension (18.4 mJ/m^2), that readily permeated into the grooves of the superhydrophobic surface. After the sonication, both the water contact angles and sliding angles recovered to their initial values. The recovery process with our system was very quick; only 30 s was required to restore rolling superhydrophobicity. Rapid recovery is a very important characteristic for a surface to be used for droplet manipulation. To test the reversibility of this process, we repeatedly cycled the pencil drawing and sonication steps and recorded the change in the sliding angles. Figure 6 reveals excellent reversible switching of the water droplet's mobility, between rollable and pinned, over at least four cycles.

■ CONCLUSIONS

We have developed a simple method for the fabrication of MWCNT/polybenzoxazine coatings exhibiting superhydrophobicity. These coatings were sufficiently robust that tape tests and compression experiments did not affect their superhydrophobicity. The as-prepared surfaces possessed high contact angles and very low sliding angles, allowing the rolling of water droplets and, thus, suggesting potential self-cleaning ability. We have also demonstrated a facile approach for reversibly changing the nature of the adhesion of the water droplets. The as-prepared superhydrophobic surface was patterned through drawing with a pencil to create a transition from a poorly adhesive rolling state for water droplets to a highly adhesive pinning state. The recovery of superhydrophobicity, upon sonication, was very rapid. The simplicity of these patterning techniques provides extreme flexibility for the designs of various superhydrophobic surfaces with possible use in both academic research and industrial applications.

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■ ACKNOWLEDGMENT

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